



Study of hydrothermal synthesis of MoVTeNbOx catalysts

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INTRODUCTION

Multi-metal oxides based on Mo, V, Te and Nb have been reported to achieve outstanding performance in the direct oxidation of propane to acrylic acid.

Among the different crystalline phases that can be formed in MoVTeNbOx systems, the so-called M1 has shown the best catalytic performance in terms of acrylic acid selectivity and stability under reaction conditions [1,2].

Synthetic routes for the preparation of phase pure M1 are still not well understood. In particular, hydrothermal synthesis has been proved to be crucial in the formation of nano-structured M1 phase [3].

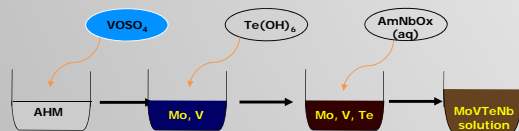
OBJECTIVE

In this work, we have studied the kinetics of precursor phase formation during the hydrothermal synthesis of mixed Mo-V-Te-Nb oxides.

The characterization of the reaction intermediates by different techniques (chemical analysis, X-ray diffraction, electron microscopy, UV-vis and Raman spectroscopy) provides valuable information in order to understand and direct hydrothermal synthesis to the formation of phase-pure M1 catalysts.

EXPERIMENTAL

Preparation of aqueous solution of reactants



AHM: Ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$
AmNbOx: Ammonium niobium oxalate, $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_{22}\text{Nb}_2$

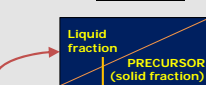
HYDROTHERMAL SYNTHESIS



175 °C, 13 bar

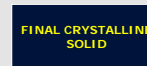
ANALYSIS OF THE REACTION INTERMEDIATES

Cool down and centrifugation of suspension



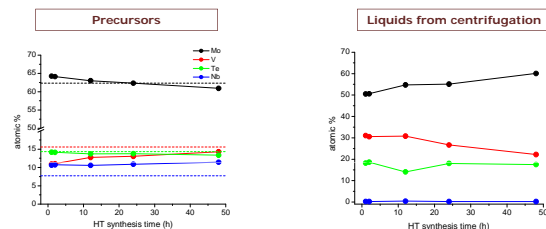
Thermal treatment

5 ml/min Ar at 625 °C, 2 h



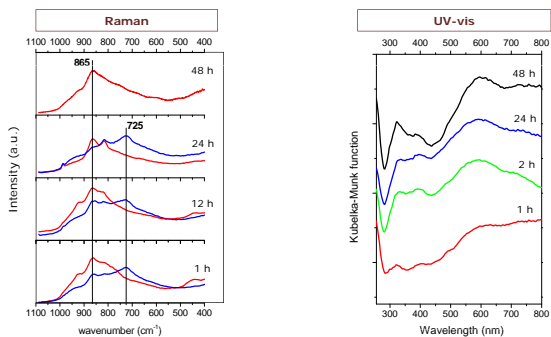
RESULTS AND DISCUSSION

Chemical composition of solid and liquid fractions



Vanadium is gradually incorporated in the solid with time under hydrothermal conditions
Nb precipitated at initial stage of reaction

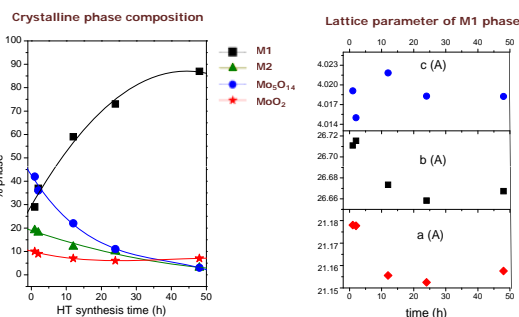
Raman and UV-vis spectra of precursors



Precursors chemically heterogeneous for $t < 48\text{h}$.
At least two different species (red and blue spectra):
 $865\text{ cm}^{-1} \rightarrow \text{Mo-O-M}$ in heteropolymolybdate (M1 building block)
 $725\text{ cm}^{-1} \rightarrow \text{Nb-O-M}$ ($M = \text{V, Mo, Te}$) in a Nb-enriched mixed oxide

Bands at 300-450 nm: change in environment of Mo^{6+} and V^{5+} species after 48 h
Weak band at 500 nm (Mo^{6+} contribution)
Band at 580 nm: Mo^{n+} ($n < 6$) species. Shift to higher wavelength in sample 48h indicates higher average oxidation state of Mo
Weak band at 725 nm: V^{4+} species for $t > 2\text{h}$

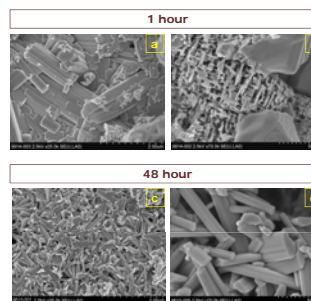
X-Ray diffraction of MoVTeNbOx catalysts



Formation of M1 with time under hydrothermal conditions at expenses of Mo_5O_{14} and M2 phases

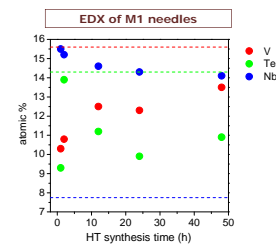
Considerably higher lattice parameter a and b for M1 phase crystallized after only 1-2 hours under hydrothermal synthesis

SEM-EDX



Size, shape and composition of M1 needles are affected by the hydrothermal reaction time.

Short-time precursors showed ill-crystallized areas (Figure b) depleted of Te (in good agreement with a higher Te loss during activation).



Total amount of Mo remained constant and close to nominal value.

Longer time under hydrothermal conditions produces a substitution of Nb by V in M1 particles.

CONCLUSIONS

- * Gradual incorporation of V in the M1 precursor, at expenses of Nb
- * Increase in the average oxidation state of Mo species, probably related to the substitution of Nb^{5+} by V^{4+}
- * Disappearance of Nb-enriched MoVTeNb oxide precursor \rightarrow solid after 48 h chemically homogeneous

* Crystallization of precursor synthesized at short times:

- A M1 phase strongly distorted (because of its high content in Nb) is formed in amounts $< 50\%$
- Important amounts of Mo_5O_{14} , M2 and ill-crystallized material (depleted in Te), that could be formed by partial decomposition of unstable Nb-rich M1 phase during the thermal treatment

Hydrothermal synthesis has a strong effect in the nature of MoVTeNbOx precursors!

It is concluded that the kinetics of formation of M1 crystalline phase are closely tied to the incorporation of V from solution into the structure of nanocrystalline precursors